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## PATENT ABSTRACTS OF JAPAN

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## (54) FLAME-RETARDANT RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a flame-retardant resin composition capable of developing excellent drop-preventing property in combustion, impact resistance, etc. by melting and kneading a specific granular masterbatch in which tetrafluoroethylene resin is contained at high concentration with a thermoplastic resin and a flame retardant.

SOLUTION: This flame-retardant resin composition is obtained by melting and kneading (A) 0.1-30 pts.wt. granular tetrafluoro masterbatch comprising (i) tetrafluoroethylene resin, (ii) powdery additive for synthetic resins and/or powdery synthetic resin and (iii) a low melting point additive for synthetic resins having lower melting point than that of the component (ii), having (0.5/99.5) to (50/50) weight ratio of the component (i)/components (ii+iii) and (1/5)/(50/1) weight ratio of the component (ii)/(iii) and obtained by mixing the component (ii) with the component (iii) at a temperature not lower than melting point of the component (iii) and mixing the component (i) therewith after starting to produce the mixed particles and having globular shape or a shape in close to globe, based on 100 pts.wt. total amount of (B) a thermoplastic resin and (C) flame retardant.

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flame retarder as (A)(iii) low m.pt.

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 PA Asahi Chemical Industry Co., Ltd., Japan  
 SO Jpn. Kokai Tokkyo Koho, 6 pp.  
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CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
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JP 2001002947	ICM	C08L101-16
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AB Title compns. comprise (A) spherical granular tetrafluoroethylene masterbatches consisting of (a-1) tetrafluoroethylene resins, (a-2) powdered additives for synthetic resins and/or powdered synthetic resins, and (a-3) low-m.p. additives for synthetic resins having lower m.p. than (a-2), which are obtained by mixing (a-2) and (a-3) while maintaining temperature higher than m.p. of (a-3) and adding (a-1) after mixed particles are started to form, where weight ratios of (a-1)/[(a-2) + (a-3)] = 0.5/99.5 - 50/50 and (a-2)/(a-3) = 1/5 - 50/1, (B) thermoplastic resins, and (C) fireproofing agents, where A = 0.1-30 parts based on 100 parts B + C. Thus, calcium carbonate 1, tris(2,4-di-tert-butylphenyl) phosphite 0.5, calcium stearate 0.4, and tri-Ph phosphate 0.21 kg were mixed at 70°, 0.25 kg Polyflon PA 500 was added to give a tetrafluoroethylene masterbatch (spherical granular, diameter 0.5-4 mm). Poly-2,6-dimethyl-1,4-phenylene ether (ηsp/c 0.54 at 30° in chloroform) 30, rubber-reinforced polystyrene 58, tri-Ph phosphate 11, tetrafluoroethylene masterbatch 1 parts were kneaded at 300° for 2 h using an extruder to give pellets and injection molded at 60° showing flame retardance (UL-94) V-1, no burning drops, tensile strength (ASTM D 638) 359 kg/cm<sup>2</sup>, elongation 58%, drop impact strength 41 J, and no PTFE deposits on the extruder, etc.

ST flame retardant resin compn contg PTFE

IT Fire-resistant materials

Fireproofing agents

(preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT Fluoropolymers, uses

RL: MOA (Modifier or additive use); USES (Uses)

(preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT Polyoxyphenylenes

RL: MOA (Modifier or additive use); POF (Polymer in formulation); PRP

(Properties); TEM (Technical or engineered material use); USES (Uses)

(preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT Polymer blends

RL: PRP (Properties); TEM (Technical or engineered material use); USES

(Uses)

(preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT Plastics, properties

RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or

engineered material use); USES (Uses)

(thermoplastics; preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT 557-05-1, Zinc stearate  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (additive; preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT 471-34-1, Calcium carbonate, uses  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (filler; preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT 115-86-6, Triphenyl phosphate  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (fireproofing agent or plasticizer; preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT 79-94-7, Tetrabromobisphenol A 1309-64-4, Antimony trioxide, uses 31870-48-1, CR 741  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (fireproofing agent; preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT 78-04-6, Dibutyltin maleate  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (heat stabilizer; preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT 1592-23-0, Calcium stearate  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (lubricant; preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT 9002-84-0, Polyflon FA 500  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT 9003-56-9 24938-67-8, Poly-2,6-dimethyl-1,4-phenylene ether 25134-01-4  
 RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)  
 (preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT 9003-53-6, Polystyrene  
 RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)  
 (rubber-reinforced; preparation of flame-retardant thermoplastic resin compns. containing PTFE)

IT 2082-79-3, Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate 31570-04-4, Tris(2,4-di-tert-butylphenyl) phosphite  
 RL: MOA (Modifier or additive use); USES (Uses)  
 (thermal stabilizer; preparation of flame-retardant thermoplastic resin compns. containing PTFE)

DERWENT-ACC-NO: 2001-310337

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TITLE: Fire-retardant resin composition, comprises  
tetrafluoroethylene master batch, thermoplastic resin,  
and flame-retardant agent

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ABSTRACTED-PUB-NO: JP2001002947A

BASIC-ABSTRACT:

NOVELTY - Fire-retardant resin composition includes: (A) a tetrafluoroethylene master batch; (B) a thermoplastic resin; and (C) a flame retardant agent.

DETAILED DESCRIPTION - Fire-retardant resin composition includes: (A) a tetrafluoroethylene master batch consisting:

(a-1) a tetrafluoroethylene resin;

(a-2) a powdery additive for a synthetic resin and/or a powdery synthetic resin; and

(a-3) an additive for a synthetic resin with a melting point lower than that of the powdery additive (a-2), provided that (a-1)/(a-2)/(a-3) = 1/5 approx. 50/1;

(B) a thermoplastic resin; and

(C) a flame retardant.

Master batch (A) is obtained by mixing (a-2) with (a-3) where the system is kept at a temperature not less than the melting point of (a-3). (a-1) is mixed into the mixture after mixed particles of (a-2) and (a-3) begin to be form.

USE - None is given.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: FIRE RETARD RESIN COMPOSITION COMPRISE MASTER BATCH THERMOPLASTIC  
RESIN FLAME RETARD AGENT

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]** This invention relates to the fire-resistant resin constituent with which handling comes to blend an easy tetrafluoroethylene masterbatch, without condensing according to external force.

**[0002]**

**[Description of the Prior Art]** It is known that effectiveness of tetrafluoroethylene resin (it is hereafter described as PTFE.) is large as the dropping prevention in flameproofing and abrasiveness amelioration of thermoplastics by carrying out little addition to thermoplastics.

**[0003]** Generally, when adding PTFE to thermoplastics, since the melting point of PTFE is higher than the working temperature of thermoplastics, it kneads below with the melting point of PTFE. It is said that PTFE by which PTFE fibrosed easily by receiving shearing force, or was easy to condense it, and kneading addition was carried out at thermoplastics fibroses in the shape of a network, and demonstrates effectiveness, such as dropping prevention. However, such fibrosis, and the condensation ease of carrying out of PTFE are dramatically troublesome on handling, and the improvement technique of handling nature is proposed variously. For example, the method of processing and using PTFE for a open patent official report common 10-30046 with the dispersant of higher fatty acids beforehand is proposed.

**[0004]** Generally, since PTFE is fine particles, when fine particles as it is are used, produce contamination of the work environment by scattering, or In case it mixes with thermoplastics, on the occasion of supply to an extruder, produce the blocking high which PTFE condenses since it has the above-mentioned property, or It generated, also when resulting in the situation it is not only difficult, but where adhering to the wall and screw of a feeder or an extruder, and it being stabilized, and carrying out supply kneading cannot carry out blinding to the screen with which the extruder die head was equipped, and cannot continue extrusion. Moreover, since the resin constituent which it kneaded by doing in this way did not have the good dispersibility of PTFE, the aggregate of PTFE was often observed on the surface of the cast, and it had the trouble of impact strength falling.

**[0005]** In order to deal with it conventionally on the other hand and to raise a sex, the granular constituent which contains PTFE in high concentration is examined, and the granular PTFE constituent is indicated by a open patent official report common 09-324124, common [ 09-324071 ], common [ 09-324072 ], common [ 09-324073 ], common [ 09-324074 ], common [ 09-324092 ], and common [ 09-324093 ]. However, in the technique indicated in these patent official reports, the dispersibility of PTFE was not enough, and it was difficult to carry out long duration continuation of the extrusion kneading, and there was a problem of the engine performance fully not being demonstrated.

**[0006]**

**[Problem(s) to be Solved by the Invention]** The object of this invention is solving the trouble on the property of the fire-resistant resin constituent containing the trouble and PTFE at the time of blending PTFE with thermoplastics in view of the above-mentioned problem, and it is in offering the fire-resistant

resin constituent excellent in the dropping tightness at the time of combustion, shock resistance, an appearance, etc.

[0007]

[Means for Solving the Problem] this invention persons resulted that the object was attained in a header and this invention by carrying out melting kneading of the specific granular tetrafluoroethylene masterbatch which PTFE contained in high concentration with thermoplastics and a flame retarder, as a result of examining wholeheartedly the fire-resistant resin constituent excellent in the dropping tightness at the time of combustion, shock resistance, an appearance, etc.

[0008] This invention Namely, the powder additive and/or powder synthetic resin (a-2) for tetrafluoroethylene resin (a-1) and synthetic resin, And (a-2) it consists of the low-melt point point additive for synthetic resin (a-3) which has the low melting point. The weight ratio of (a-1)/(a-2) (+ (a-3)) 0.5 / the range of 99.5 - 50/50, And (a-2) the weight ratio of / (a-3) is in the range of 1 / 5 - 50/1. It mixes. and (a-3) more than the melting point - holding (a-2) - (a-3) After the mixed particle begins to generate, the tetrafluoroethylene masterbatch (A) of the shape of a grain which has the configuration of the globular form obtained by subsequently (a-1) mixing, or globular form approximation It is the fire-resistant resin constituent which comes to carry out 0.1-30 weight section melting kneading to thermoplastics (B) and the total quantity 100 weight section of a flame retarder (C).

[0009] The tetrafluoroethylene resin (a-1) used for this invention is a copolymer with the homopolymer of tetrafluoroethylene and tetrafluoroethylene and difluoro ethylene, trifluoro ethylene, hexafluoropropylene, etc.

[0010] The manufacture approach of these PTFE is indicated by U.S. Pat. No. 2,393,697 and U.S. Pat. No. 2,534,058, for example, the polymerization of the tetrafluoroethylene is carried out at the temperature of 0-200 degrees C under 7-70kg/cm<sup>2</sup> application of pressure using radical initiators, such as ammonium persulfate and potassium persulfate, in an aqueous medium, and, subsequently polytetrafluoroethylene powder is obtained from suspension, dispersion liquid, or an emulsion by coagulation or precipitate.

[0011] For example, an ethylene tetrafluoride monomer is used as a raw material, and it is manufactured by the emulsion-polymerization method by the radical polymerization using a peroxide, or the suspension-polymerization method. Moreover, the denaturation type which replaced some fluorine atoms by an another substituent or an another element is also used. Although PTFE obtained by this approach takes the gestalt of fine particles or dispersion, what fibroses in the shape of a network easily [ become altitude with a crystalline substance and ] is desirable.

[0012] The powder additive for synthetic resin (a-2) used for this invention is an additive powdery in the ordinary temperature generally blended and used for thermoplastic synthetic resin, and an inorganic bulking agent, a coloring agent, a thermostabilizer, lubricant, a flame retarder, an antistatic agent, an ultraviolet ray absorbent, etc. are mentioned, and it can also use two or more sorts together. In it, a high-melting additive 100 degrees C or more has especially desirable inorganic bulking agent and melting point.

[0013] Although the powdery synthetic resin (a-2) used for this invention was generally obtained as a powdery polymer, what ground resin massive otherwise can use it.

[0014] The low-melt point point additive (a-3) used for this invention is required as a binders of the powdered material for granulating, and even after granulating, the role of the excipient which makes the grain shape of the mixture hold is played. As the concrete additive, a plasticizer, a thermostabilizer, lubricant, a flame retarder, an antistatic agent, an ultraviolet ray absorbent, oligomer, etc. are mentioned, and two or more sorts can also be used together.

[0015] As for a low-melt point point additive (a-3), what needs to have the melting point or softening temperature lower than a powder additive (a-2) for synthetic resin, and has the melting point of 100 degrees C or less beyond ordinary temperature from the ease of making is desirable. Since the melting point is below ordinary temperature and becomes soft [ in the front face of the done granular tetrafluoroethylene resin constituent being sticky as the amount of a liquefied object increases, although used together and used ] independently [ a liquefied thing ] in ordinary temperature, storage nature and

handling nature are inferior.

[0016] In order to obtain the tetrafluoroethylene masterbatch (A) of the shape of a grain which has the configuration of the globular form used for this invention, or globular form approximation The high-speed mixer of the structure where the inside of a tub can be held is used for the constant temperature according to the high speed mixer with a jacket or it which was known as a Henschel mixer and a super mixer. The approach of granulating by mixing the above-mentioned component in the following procedures is desirable, and the approach of using a high speed mixer as an only mixer, and also using together a high speed mixer and other high-speed-shearing agitators is also used.

[0017] that time -- the jacket of a high speed mixer -- more than the melting point of a low-melt point (a-3) point additive -- holding (a-2) -- after it mixes and the mixed particle begins to generate, it is desirable to supply PTFE subsequently (a-1) and to mix for a short time (a-3). Thus, the granular mixture containing obtained PTFE is presumed to be what takes the structure which used as the inner shell the granular object which contained (a-3) as an excipient (a-2), almost all particles have the configuration of a globular form or globular form approximation as a result, and the magnitude of the particle is obtained from the diameter of about 0.1mm to an about 5mm thing according to the class of component, a presentation, and mixed conditions. The configuration of the globular form in this invention or globular form approximation points out a configuration at large [ near a ball ], and the ellipse ball near the Rugby ball is also contained, and the front face of a particle is not necessarily smooth.

[0018] each component (a-1) which constitutes the tetrafluoroethylene masterbatch (A) of the shape of a grain which has the configuration of the globular form used for this invention, or globular form approximation -- and (a-2) (a-3) a rate Although what kind of rate is sufficient as long as it can granulate, for the weight ratio of (a-1)/(a-2) (+ (a-3)), as desirable range which can be granulated, the range of the range of 0.5 / 99.5 - 50/50 and (a-2) the weight ratio of / (a-3) is 1 / 5 - 50/1. For the weight ratio of (a-1)/(a-2) (+ (a-3)), the range of the range of 1 / 99 - 20/80 and (a-2) the weight ratio of / (a-3) of the more desirable range from the ease of manufacturing is 2 / 1 - 20/1.

[0019] It is the tetrafluoroethylene masterbatch excellent in the handling nature which the tetrafluoroethylene masterbatch (A) used by this invention does not have scattering or condensation of PTFE, and adhesion to processing equipment does not have, either, and the fire-resistant resin constituent of this invention excellent in fire retardancy, shock resistance, an appearance, etc. can be obtained by carrying out melting mixing with thermoplastics (B) and a flame retarder (C). the rate of each component -- thermoplastics (B) and the total quantity 100 weight section of a flame retarder (C) -- receiving -- a tetrafluoroethylene masterbatch (A) -- the range of 0.1 - 30 weight section -- it is the range of 0.5 - 10 weight section preferably. In order to obtain the fire-resistant resin constituent of this invention, it is important for a fire-resistant resin constituent as PTFE 0.01 - 2 weight section and to recognize 0.02-1 weight section existence preferably, not only worsening \*\*\*\*\* and the appearance of machine physical properties but in below the 0.01 weight sections, there is no dropping prevention effectiveness at the time of combustion, and more than 2 weight sections are economically disadvantageous.

[0020] As thermoplastics (B) used for this invention, various kinds of homopolymer, copolymers and these rubber consolidation polymers, or polymer alloys are mentioned, and it does not restrict especially. As a concrete example, the things which reinforced the homopolymer of vinyl compounds, such as polystyrene, a styrene acrylonitrile copolymer, and polymethylmethacrylate, and a copolymer, polyethylene, polypropylene, polyphenylene ether, polyethylene terephthalate, polybutylene terephthalate, a polycarbonate, a polyamide, and these with the gum polymer, and these polymer alloys are mentioned.

[0021] As a flame retarder (C) used for this invention, if generally used as fire retardancy of inflammable thermoplastics, all can be used, for example, the flame retarder of a halogen system and the Lynn system will be mentioned.

[0022] As a halogen series flame retardant, an aromatic series halogenated compound, a halogenated-aromatics system polymer, Halogenation SHIANU rate resin etc. is mentioned. Preferably A bromine-ized bisphenol system epoxy resin, Bromine-ized bisphenol system phenoxy resin, bromine-ized

bisphenol system polycarbonate resin, Bromine-ized polystyrene resin, bromine-ized bridge formation polystyrene resin, bromine-ized bisphenol SHIANU rate resin, Bromine-ized polyphenylene ether, deca BUROMO diphenyloxide, tetrabromobisphenol A and its oligomer, a bromine-ized alkyl triazine compound, etc. are mentioned.

[0023] As a phosphorus series flame retardant, for example Moreover, trimethyl phosphate, triethyl phosphate, TORIPURO pill phosphate, tributyl phosphate, tripentyl phosphate, an ibis - hexyl phosphate, tricyclohexyl phosphate, and triphenyl phosphate - Tricresyl phosphate, trixylenyl phosphate, cresyl diphenyl phosphate, Dicresyl phenyl phosphate, dimethyl ethyl phosphate, methyl dibutyl phosphate, The compound which denaturalized phosphoric ester, such as ethyl dipropyl phosphate and hydroxyphenyl diphenyl phosphate, and these by various substituents, Although compounds, such as a phosphazene derivative containing a phosphoric ester compound condensation type [ various kinds of ], and Lynn and nitrogen, or mixture is mentioned, a condensed-phosphoric-acid ester compound is desirable.

[0024] The desirable phosphoric ester compound as a flame retarder (C) has the geometry by "the specific 2 organic-functions phenol", and the end structure by "the specific monofunctional phenol." As "a specific 2 organic-functions phenol", although bisphenols, such as resorcinol, hydroquinone, 2, and 2-screw (4-hydroxyphenyl) propane [common-name bisphenol A], 2, and 2-screw (4-hydroxy-3-methylphenyl) propane, screw (4-hydroxyphenyl) methane, screw (4-hydroxy - 3, 5-dimethylphenyl) methane, 1, and 1-screw (4-hydroxyphenyl) ethane, are mentioned, it is not limited to this. Especially bisphenol A is desirable.

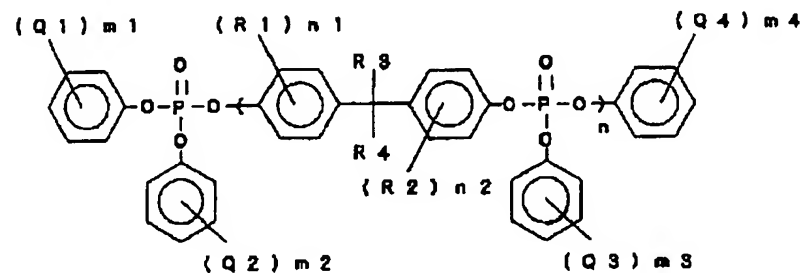
[0025] As "a specific monofunctional phenol", a non-permuted phenol, a monoalkyl phenol, a dialkyl phenol, and a trialkyl phenol can be used as independent or two or more sorts of mixture. A phenol, cresol, dimethylphenol (mixed xylene), 2, 6-dimethylphenol, and a trimethyl phenol are especially desirable.

[0026] these Lynn system compounds are independent -- or two or more sorts can be combined and it can use.

[0027] In these, especially the phosphoric ester compound expressed with a general formula (I) is desirable.

[0028]

[Formula 1]  
一般式 (I)



[0029] (Q1, Q2, Q3, and Q4 express the alkyl group of carbon numbers 1-6, or hydrogen among a formula, and R1, R2, R3, and R4 express a methyl group or hydrogen.) n shows one or more integers, n1 and n2 show the integer of 0 to 2, and m1, m2, m3, and m4 show the integer of 1 to 3. It is expressed.

[0030] Especially a desirable thing is hydrogen or a methyl group among Q1, Q2, Q3, and Q4 in a general formula (I).

[0031] Hydrogen is desirable at R1 and R2 in a general formula (I), and a \*\* methyl group is desirable at R3 and R4.

[0032] n in a general formula (I) is one or more integers, and thermal resistance and workability change with the numbers. The range of desirable n is 1-5. Moreover, this phosphoric ester may be the mixture of n \*\*\*\*.



[0033] In the resin constituent of this invention, since the property of further others is given, stabilizers, such as fibrous reinforcements, such as other additives, for example, various inorganic bulking agents, a glass fiber, and carbon fiber, a plasticizer, an antioxidant, and an ultraviolet ray absorbent, an antistatic agent, a release agent, dyes and pigments, or other resin can be added in the range which does not spoil the effectiveness of this invention.

[0034] Especially the manufacture approach of the fire-resistant resin constituent of this invention cannot be specified, and can be manufactured by carrying out melting kneading using kneading machines, such as an extruder, a heating roller, a kneader, and a Banbury mixer. Kneading by the extruder is desirable in respect of productivity also in it.

[0035]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to the following examples.

[0036]

[The example 1 of manufacture] The super mixer (made in the Kawada factory) with a jacket of 20l. of inner capacity is used. At the place which warmed the jacket with 70-degree C warm water 1kg (inorganic bulking agent) of calcium carbonates with a mean particle diameter [ as a component (a-2) ] of about 4micro, Tris (2, 4-G t-buthylphenyl) phosphite (thermostabilizer made from tiba SUPESCHARUTI KEMIKARUZU) 0.5kg, and 0.4kg (lubricant) of powdery calcium stearates, (a-3) Triphenyl phosphate (flame-retarder or plasticizer) 0.21kg as a component is taught, and it mixes by 600rpm.

[0037] Whenever [ content temperature ] amounted to 70 degrees C, dusting was subsided, 0.25kg (the Daikin Industries make, trade name Pori Flon FA 500) of PTFE (a-1) fine powder was thrown in in the place which became grain-like, and mixing was continued about further 5 minutes. Most contents were granular objects (it considers as the tetrafluoroethylene masterbatch -1.) of globular form resemblance with a diameter of about 0.5-4mm.

[0038]

[The example 2 of manufacture] The super mixer (made in the Kawada factory) with a jacket of 20l. of inner capacity is used. At the place which warmed the jacket with 70-degree C warm water Powdery polyphenylene ether 1.0kg as a component (a-2), Tris (2, 4-G t-buthylphenyl) phosphite (thermostabilizer made from tiba SUPESCHARUTI KEMIKARUZU) 0.5kg, and 0.5kg of powdery zinc stearates, (a-3) OKUDAESHIRU-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate (thermostabilizer made from tiba SUPESCHARUTI KEMIKARUZU) 0.25kg as a component is taught, and it mixes by 600rpm.

[0039] Whenever [ content temperature ] amounted to 70 degrees C, dusting was subsided, 0.25kg of PTFE (a-1) fine powder was thrown in in the place which became grain-like, and mixing was continued about further 5 minutes. Most contents were granular objects (it considers as the tetrafluoroethylene masterbatch -2.) of globular form resemblance with a diameter of about 0.2-1mm.

[0040]

[Example 1] Det.sp/c measured with the 30-degree C chloroform solution Polly 2 of 0.54, the 6-dimethyl -1, and 4-phenylene ether 30 weight sections, The tetrafluoroethylene masterbatch -1 of 11 weight sections and the example 1 of manufacture for 58 weight sections and triphenyl phosphate at a rate of 1 weight section [ the rubber reinforcement polystyrene whose volume average rubber particle diameter of about 9% of rubber contents is about 1.5 micrometers ] The twin screw extruder with a screw diameter of 40mm which set the maximum temperature of a heating cylinder as 300 degrees C was supplied, and melting kneading was continuously carried out by screw-speed 300rpm for about 2 hours. Cooling decision of the strand was carried out and the resin constituent pellet was obtained. Extrusion nature was good, without carrying out blinding, although the die head of an extruder was equipped with the screen of 200 meshes in the meantime.

[0041] The injection molding machine with a mold clamp pressure of 80t set as the cylinder temperature of 240 degrees C and the die temperature of 60 degrees C in the obtained resin constituent pellet performed injection molding, and the object sex-test piece was obtained. A fire-resistant trial and the

object sex test were performed by the method of examining the following, and the result of a table 1 was obtained.

[0042] (1) Fire-resistant trial UL-94 The injection-molding test piece of \*\*\*\*\* and 1/16 inch thickness was used and measured to the vertical firing trial. A rank V-0 is most excellent, and inferior in order of V-1, V-2, and HB.

[0043] (2) Hauling trial ASTM Tensile strength and ductility were measured based on D638.

[0044] (3) The general absorption energy value (J: joule) as falling weight impact strength was measured using the plate shaping piece with a 50mm x90mmx thickness [ of drop impact tests ] of 2.5mm with made in Oriental Energy Machine Factory, the trade name, and the graphic impact circuit tester.

[0045] (4) The visual judgment of the plate with a 50mmx90mmx thickness of 2.5mm by which appearance injection molding was carried out was carried out, and the dispersibility of PTFE was evaluated. When the aggregate of PTFE was not seen and O and an aggregate were seen, it considered as x.

[0046]

[Example 2] In the example 1, melting kneading was similarly performed except having replaced with 14 weight sections and the tetrafluoroethylene masterbatch -1 the phosphorus series flame retardant (the product made from the Daihachi chemistry, a trade name CR 741) which replaces with triphenyl phosphate and uses a condensation type phosphoric ester compound as a principal component, and having made the tetrafluoroethylene masterbatch -2 of the example 2 of manufacture into 1 weight section. Extrusion nature was good, without carrying out blinding of the screen. The obtained resin constituent pellet was similarly estimated as the example 3, and the result of a table 1 was obtained.

[0047]

[The example 1 of a comparison] In the example 1, it replaced with the tetrafluoroethylene masterbatch -1, the reserve mixture of the weight ratios 1/4 of PTFE fine powder (the Daikin Industries make, trade name Pori Flon FA 500) and calcium stearate was supplied to the 0.5 weight section and a twin screw extruder, and melting kneading was carried out in screw-speed 300rpm. Although the die head of an extruder was equipped with the screen of 200 meshes, the resin pressure of a die head rose by blinding like kneading initiation 5 minute, and continuation of extrusion operation was not completed.

[0048] Next, by replacing a screen with 40 meshes with a coarse eye, extruding it, and operating, cooling decision of the strand was carried out and the resin constituent pellet was obtained. The obtained pellet was similarly estimated as the example 1, and the result of a table 1 was obtained.

[0049]

[The example 2 of a comparison] In the example 2, by extruding similarly [ without blending the tetrafluoroethylene masterbatch -1 ], and operating, cooling decision of the strand was carried out and the resin constituent pellet was obtained. The obtained pellet was similarly estimated as the example 1, and the result of a table 1 was obtained.

[0050]

[Example 3] At 15 % of the weight of contents of polybutadiene, the ABS-plastics 100 weight section of styrene / acrylonitrile =75 / 25 (weight ratio) is received. 19 weight sections and an antimony trioxide for tetrabromobisphenol A as a flame retarder Three weight sections, As a thermostabilizer the tetrafluoroethylene masterbatch -1 of the example 1 of manufacture to the 0.5 weight section and a pan for dibutyltin maleate at a rate of 3 weight sections The twin screw extruder with a screw diameter of 30mm which set the maximum temperature of a heating cylinder as 240 degrees C was supplied, and melting kneading was continuously carried out by screw-speed 150rpm for about 2 hours. Cooling decision of the strand was carried out and the resin constituent pellet was obtained. Extrusion nature was good, without carrying out blinding, although the die head of an extruder was equipped with the screen of 200 meshes in the meantime.

[0051] The injection molding machine with a mold clamp pressure of 80t set as the cylinder temperature of 220 degrees C and the die temperature of 60 degrees C in the obtained resin constituent pellet performed injection molding, and the object sex-test piece was obtained. A fire-resistant trial and the

object sex test were performed by the above-mentioned examining method, and the result of a table 1 was obtained.

[0052]

[A table 1]

表 1

	実施例 3	比較例 1	比較例 2	実施例 4	実施例 5
<b>押出性</b>					
PTFE の付着 <sup>1)</sup>	無し	多い	—	無し	無し
スクリューの目詰まり	無し	有り	—	無し	無し
<b>物 性</b>					
難燃性 ランク	V-1	HB <sup>2)</sup>	V-2	V-1	V-0
滴 下	無し	無し	有り	無し	無し
引張強度 (kg/cm <sup>2</sup> )	359	350	347	480	—
伸 度 (%)	68	35	62	70	—
落錘衝撃強度 (J)	41	32	42	40	—
外 観	○	×	○	○	○

1) PTFE の付着：フィーダーおよび押出機のホッパー、スクリュー等への PTFE の付着凝集。

2) HB：最大燃焼時間が規定の時間以上であった。

[0053]

[Effect of the Invention] The trouble on the handling at the time of this invention blending PTFE with thermoplastics, Namely, by having prevented troubles, such as adhesion condensation to the hopper screw of condensation of PTFE, a feeder, and an extruder etc., and clogging of the screen with which the extruder die head was equipped, and having improved the dispersibility of PTFE The trouble on the property of the fire-resistant resin constituent containing conventional PTFE can be solved, and the fire-resistant resin constituent excellent in the dropping tightness at the time of combustion, shock resistance, an appearance, etc. can be offered.

[Translation done.]

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**CLAIMS**

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[Claim(s)]

[Claim 1] The powder additive and/or powder synthetic resin (a-2) for tetrafluoroethylene resin (a-1) and synthetic resin, And (a-2) it consists of the low-melt point point additive for synthetic resin (a-3) which has the low melting point. The weight ratio of (a-1)/(a-2) (+ (a-3)) 0.5 / the range of 99.5 - 50/50, And (a-2) the weight ratio of / (a-3) is in the range of 1 / 5 - 50/1. It mixes. and (a-3) more than the melting point -- holding (a-2) -- (a-3) After the mixed particle begins to generate, the tetrafluoroethylene masterbatch (A) of the shape of a grain which has the configuration of the globular form obtained by subsequently (a-1) mixing, or globular form approximation The fire-resistant resin constituent which comes to carry out 0.1-30 weight section melting kneading to thermoplastics (B) and the total quantity 100 weight section of a flame retarder (C).

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[Translation done.]

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(54) 【発明の名称】 難燃樹脂組成物

(57) 【要約】

【課題】 本発明の目的は、PTFEを熱可塑性樹脂に配合する際の問題点やPTFEを含有する難燃樹脂組成物の特性上の問題点を解決することであり、難燃性、耐衝撃性、外観等に優れた難燃樹脂組成物を提供することにある。

【解決手段】 あらかじめ粉状添加剤および／または粉状樹脂と低融点添加剤とを混合し混合粒子を形成した後、PTFEを混合して得た特定の粒状テトラフルオロエチレンマスターバッチを熱可塑性樹脂および難燃剤と溶融混練りしてなる難燃樹脂組成物。

## 【特許請求の範囲】

【請求項1】 テトラフルオロエチレン樹脂(a-1)、合成樹脂用の粉状添加剤および/または粉状合成樹脂(a-2)、および(a-2)よりも低い融点を有する合成樹脂用の低融点添加剤(a-3)から成り、 $(a-1)/((a-2)+(a-3))$ の重量比が0.5/99.5~50/50の範囲、および $(a-2)/(a-3)$ の重量比が1/5~50/1の範囲にあり、かつ(a-3)の融点以上に保持して(a-2)と(a-3)とを混合し、その混合粒子が生成し始めた後、次いで(a-1)を混合することにより得られた球形または球形近似の形状を有する粒状のテトラフルオロエチレンマスターバッチ(A)を、熱可塑性樹脂(B)および難燃剤(C)の合計量100重量部に対して、0.1~30重量部溶融混練りしてなる難燃樹脂組成物。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、外力により凝集することなく、取り扱いが容易なテトラフルオロエチレンマスターバッチを配合してなる難燃樹脂組成物に関する。

【0002】

【従来の技術】テトラフルオロエチレン樹脂(以下、PTFEと記述する。)は、熱可塑性樹脂に少量添加することにより、熱可塑性樹脂の難燃化における滴下防止や摩耗性改良として効果が大いことが知られている。

【0003】一般に、熱可塑性樹脂にPTFEを添加する場合は、PTFEの融点が熱可塑性樹脂の加工温度より高いためにPTFEの融点以下で混練りされる。PTFEは、剪断力を受けることにより容易に繊維化したり凝集し易く、熱可塑性樹脂に混練り添加されたPTFEは、ネットワーク状に繊維化して滴下防止などの効果を発揮すると言われている。しかしながら、PTFEのこのような繊維化や凝集し易さは、取り扱いの上では非常に厄介であり、取り扱い性の向上技術が種々提案されている。例えば、公開特許公報平10-30046にはPTFEを予め、高級脂肪酸類の分散剤で処理して用いる方法が提案されている。

【0004】一般的に、PTFEは粉体であるため、そのままの粉体を用いた場合には飛散による作業環境の汚染を生じたり、熱可塑性樹脂と混合する際、成いは押出機への供給に際し、上記の性質を有するためにPTFE同士が凝集するブロッキング現象を生じたり、供給装置や押出機の内壁やスクリュウに付着し、安定して供給混練りすることが難しいだけでなく、押出機ダイヘッドに装着したスクリーンに目詰まりして押出を続けることができない事態に至る場合も発生した。また、このようにして混練りされた樹脂組成物は、PTFEの分散性が良くないために成型品の表面にPTFEの凝集物がしばし

ば観察され、衝撃強度が低下するなどの問題点を有していた。

【0005】一方従来より取り扱い性を向上させるために、PTFEを高濃度に含有する粒状組成物が検討され、公開特許公報平09-324124、平09-324071、平09-324072、平09-324073、平09-324074、平09-324092、平09-324093などには粒状PTFE組成物が開示されている。しかしながら、これらの特許公報で開示された技術においてもPTFEの分散性は充分ではなく、押出混練りを長時間継続することが困難であったり、性能が充分に発揮されないなどの問題があった。

【0006】

【発明が解決しようとする課題】本発明の目的は上記問題に鑑み、PTFEを熱可塑性樹脂に配合する際の問題点やPTFEを含有する難燃樹脂組成物の特性上の問題点を解決することであり、燃焼時の滴下防止性、耐衝撃性、外観等に優れた難燃樹脂組成物を提供することにある。

【0007】

【課題を解決するための手段】本発明者らは燃焼時の滴下防止性、耐衝撃性、外観等に優れた難燃樹脂組成物を鋭意検討した結果、PTFEが高濃度に含有された特定の粒状テトラフルオロエチレンマスターバッチを熱可塑性樹脂および難燃剤と溶融混練りすることにより目的が達成されることを見出し、本発明に至った。

【0008】すなわち本発明は、テトラフルオロエチレン樹脂(a-1)、合成樹脂用の粉状添加剤および/または粉状合成樹脂(a-2)、および(a-2)よりも低い融点を有する合成樹脂用の低融点添加剤(a-3)から成り、 $(a-1)/((a-2)+(a-3))$ の重量比が0.5/99.5~50/50の範囲、および $(a-2)/(a-3)$ の重量比が1/5~50/1の範囲にあり、かつ(a-3)の融点以上に保持して(a-2)と(a-3)とを混合し、その混合粒子が生成し始めた後、次いで(a-1)を混合することにより得られた球形または球形近似の形状を有する粒状のテトラフルオロエチレンマスターバッチ(A)を、熱可塑性樹脂(B)および難燃剤(C)の合計量100重量部に対して、0.1~30重量部溶融混練りしてなる難燃樹脂組成物である。

【0009】本発明に用いられるテトラフルオロエチレン樹脂(a-1)は、テトラフルオロエチレンの単独重合体およびテトラフルオロエチレンとジフルオロエチレン、トリフルオロエチレン、ヘキサフルオロプロピレン等との共重合体である。

【0010】これらのPTFEの製造方法は、米国特許第2,393,697号および米国特許第2,534,058号に開示され、例えばテトラフルオロエチレンを水性媒体中で過硫酸アンモニウム、過硫酸カリウム等の

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ラジカル開始剤を用いて、7~70 kg/cm<sup>2</sup>の加圧下、0~200℃の温度で重合し、次いで懸濁液、分散液または乳濁液から凝析により、または沈殿によりポリテトラフルオロエチレン粉末が得られる。

【0011】例えば、4フッ化エチレンモノマーを原料とし、過酸化剤を用いたラジカル重合による乳化重合法、もしくは懸濁重合法により製造される。また、フッ素原子の一部を別の置換基もしくは元素で置き換えた変性タイプも用いられる。この方法によって得られるPTFEは、粉体もしくはディスパーションの形態を取るが、高度に結晶質となりかつ容易にネットワーク状に繊維化するものが好ましい。

【0012】本発明に用いられる合成樹脂用の粉状添加剤(a-2)は、一般に熱可塑性合成樹脂に配合して用いられる常温で粉状の添加剤であって、無機充填剤、着色剤、熱安定剤、滑剤、難燃剤、帯電防止剤、紫外線吸収剤などが挙げられ、2種以上を併用することもできる。その中で、特に無機充填剤や融点が100℃以上の高融点添加剤が好ましい。

【0013】本発明に用いられる粉状の合成樹脂(a-2)は、一般に粉状の重合体として得られたものの他に塊状の樹脂を粉砕したものも用いることができる。

【0014】本発明に用いられる低融点添加剤(a-3)は、粒状化するに際しての粉状物の粘着剤として必要であり、粒状化した後もその混合物の粒形を保持させる賦形剤の役割を果たしている。その具体的な添加剤としては、可塑剤、熱安定剤、滑剤、難燃剤、帯電防止剤、紫外線吸収剤、オリゴマーなどが挙げられ、2種以上を併用することもできる。

【0015】低融点添加剤(a-3)は合成樹脂用の粉状添加剤(a-2)よりも低い融点または軟化点をもつ必要があり、作り易さから常温以上100℃以下の融点をもつものが好ましい。融点が常温以下であり常温では液状のものも単独または併用して用いられるが、液状物の量が多くなるにしたがい、できあがった粒状テトラフルオロエチレン樹脂組成物の表面がべとついたり、柔らかくなるために保管性や取り扱い性が劣るものとなる。

【0016】本発明に用いられる球形または球形近似の形状を有する粒状のテトラフルオロエチレンマスターバッチ(A)を得るには、ヘンシェルミキサー、スーパーミキサーとして知られたジャケット付きの高速ミキサーあるいはそれに準じた一定温度に槽内を保持できる構造の高速混合機を用いて、上記成分を以下の手順で混合することにより粒状化する方法が好ましく、高速ミキサーを唯一の混合機として用いる他に、高速ミキサーと他の高速剪断攪拌機を併用する方法も用いられる。

【0017】その際、高速ミキサーのジャケットを(a-3)低融点添加剤の融点以上に保持して(a-2)と(a-3)とを混合し、その混合粒子が生成し始めた後、次いで(a-1) PTFEを投入して短時間で混合

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することが望ましい。このようにして得られたPTFEを含有する粒状混合物は、(a-3)を賦形剤として含有した(a-2)との粒状物を内殻とした構造を取るものと推定され、結果としてほとんどの粒子が球形または球形近似の形状を有し、その粒子の大きさは成分の種類、組成および混合条件により直径0.1 mm程度から5 mm程度のものまで得られる。本発明における球形または球形近似の形状とは、球に近い形状全般を指し、ラグビーボールに近い楕円球も含まれ、また粒子の表面は必ずしも滑らかではない。

【0018】本発明に用いられる球形または球形近似の形状を有する粒状のテトラフルオロエチレンマスターバッチ(A)を構成する各成分(a-1)、(a-2)および(a-3)の割合は、粒状化することができればいかなる割合でも構わないが、粒状化できる好ましい範囲としては、(a-1)/((a-2)+(a-3))の重量比が0.5/99.5~50/50の範囲、および(a-2)/(a-3)の重量比が1/5~50/1の範囲である。製造し易さからのより好ましい範囲は、(a-1)/((a-2)+(a-3))の重量比が1/99~20/80の範囲、および(a-2)/(a-3)の重量比が2/1~20/1の範囲である。

【0019】本発明で用いられるテトラフルオロエチレンマスターバッチ(A)は、PTFEの分散や凝集がなく、加工装置への付着もない取り扱い性に優れたテトラフルオロエチレンマスターバッチであり、熱可塑性樹脂(B)および難燃剤(C)とともに熔融混合することにより難燃性、耐衝撃性、外観等に優れた本発明の難燃樹脂組成物を得ることができる。各成分の割合は、熱可塑性樹脂(B)および難燃剤(C)の合計量100重量部に対し、テトラフルオロエチレンマスターバッチ(A)が0.1~30重量部の範囲、好ましくは0.5~10重量部の範囲である。本発明の難燃樹脂組成物を得るには、難燃樹脂組成物にPTFEとして0.01~2重量部、好ましくは0.02~1重量部存在することが重要であり、0.01重量部以下では燃焼時の滴下防止効果がなく、2重量部以上は機械物性にて低下や外観を悪化させるだけでなく経済的に不利である。

【0020】本発明に用いられる熱可塑性樹脂(B)としては、各種のホモポリマー、コポリマーおよびこれらのゴム強化ポリマー或いはポリマーアロイが挙げられ、特に制限するものではない。具体的例としては、ポリスチレン、スチレン-アクリロニトリル共重合体、ポリメチルメタクリレート等のビニル化合物の単独重合体および共重合体、ポリエチレン、ポリプロピレン、ポリフェニレンエーテル、ポリエチレンテレフタレート、ポリブチレンテレフタレート、ポリカーボネート、ポリアミドおよびこれらをゴム質重合体で補強したもの、およびこれらのポリマーアロイが挙げられる。

【0021】本発明に用いられる難燃剤(C)として

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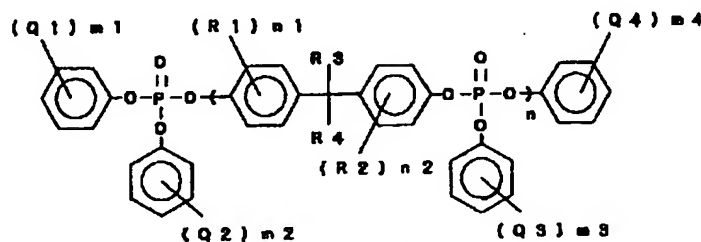
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は、一般に可燃性の熱可塑性樹脂の燐燐として用いられるものであればいずれも用いることができ、例えばハロゲン系、リン系の燐燐が挙げられる。

【0022】ハロゲン系燐燐としては芳香族ハロゲン化合物、ハロゲン化芳香族系重合体、ハロゲン化シアヌレート樹脂等が挙げられ、好ましくはブロム化ビスフェノール系エポキシ樹脂、ブロム化ビスフェノール系フェノキシ樹脂、ブロム化ビスフェノール系ポリカーボネート樹脂、ブロム化ポリスチレン樹脂、ブロム化架橋ポリスチレン樹脂、ブロム化ビスフェノールシアヌレート樹脂、ブロム化ポリフェニレンエーテル、デカブロモジフェニルオキサイド、テトラブロモビスフェノールAおよびそのオリゴマー、ブロム化アルキルトリアジン化合物などが挙げられる。

【0023】また、リン系燐燐としては、例えばトリメチルホスフェート、トリエチルホスフェート、トリプロピルホスフェート、トリブチルホスフェート、トリペンチルホスフェート、トキヘキシルホスフェート、トリシクロヘキシルホスフェート、トリフェニルホスフェート、トリクレジルホスフェート、トリキシレニルホスフェート、クレジルジフェニルホスフェート、ジクレジルフェニルホスフェート、ジメチルエチルホスフェート、メチルジブチルホスフェート、エチルジプロピルホスフェート、ヒドロキシフェニルジフェニルホスフェート等のリン酸エステルやこれらを各種置換基で変性した化合物、各種の縮合タイプのリン酸エステル化合物、リンと窒素を含有するホスファゼン誘導体など化合物又は混合\*  
一般式 (I)



【0029】(式中、Q1、Q2、Q3、Q4は、炭素数1から6のアルキル基、または水素を表し、R1、R2、R3、R4はメチル基、または水素を表す。nは1以上の整数を、n1、n2は0から2の整数を示し、m1、m2、m3、m4は、1から3の整数を示す。)で、表される。

【0030】一般式 (I) におけるQ1、Q2、Q3、Q4のうち特に好ましいのは水素、またはメチル基である。

【0031】一般式 (I) におけるR1、R2で好ましいのは水素であり、R3、R4で好ましいのはメチル基である。

【0032】一般式 (I) におけるnは1以上の整数で※50

\*物などが挙げられるが、縮合リン酸エステル化合物が好ましい。

【0024】燐燐 (C) としての好ましいリン酸エステル化合物は、“特定の二官能フェノール”による結合構造と“特定の単官能フェノール”による末端構造を有する。“特定の二官能フェノール”としては、レゾルシン、ハイドロキノ、2, 2-ビス(4-ヒドロキシフェニル)プロパン〔通称ビスフェノールA〕、2, 2-ビス(4-ヒドロキシ-3-メチルフェニル)プロパン、ビス(4-ヒドロキシフェニル)メタン、ビス(4-ヒドロキシ-3, 5-ジメチルフェニル)メタン、1, 1-ビス(4-ヒドロキシフェニル)エタンなどのビスフェノール類が挙げられるが、これに限定されない。特にビスフェノールAが好ましい。

【0025】“特定の単官能フェノール”としては、無置換フェノール、モノアルキルフェノール、ジアルキルフェノール、トリアルキルフェノールを単独または2種以上の混合物として使用できる。特にフェノール、クレゾール、ジメチルフェノール(混合キシレノール)、2, 6-ジメチルフェノール、トリメチルフェノールが好ましい。

【0026】これらのリン系化合物は単独あるいは2種以上組み合わせて用いることができる。

【0027】これらの中で、一般式 (I) で表されるリン酸エステル化合物が特に好ましい。

【0028】

【化1】

※あつてその数により耐熱性、加工性が異なってくる。好ましいnの範囲は1~5である。また該リン酸エステルはn量体の混合物であってもかまわない。

【0033】本発明の樹脂組成物には、更に他の特性を付与するため、または本発明の効果を損なわない範囲で他の添加剤、例えば各種無機充填剤、ガラス繊維やカーボン繊維などの繊維状強化剤、可塑剤、酸化防止剤、及び紫外線吸収剤などの安定剤、帯電防止剤、離型剤、染料、あるいはその他の樹脂を添加することができる。

【0034】本発明の燐燐樹脂組成物の製造方法は、特に規定するものではなく、押出機、加熱ロール、ニーダー、パンバリーミキサー等の混練機を用いて溶融混練することにより製造することができる。その中でも押出機



による混練りが、生産性の面で好ましい。

#### 【0035】

【実施例】以下、実施例によって本発明を具体的に説明するが、本発明は以下の例に限定されるものではない。

#### 【0036】

【製造例1】内容量20リットルのジャケット付きスーパーミキサー（川田製作所製）を用い、70℃の温水でジャケットを加温したところに、（a-2）成分としての平均粒径約4μmの炭酸カルシウム（無機充填剤）1kg、トリス（2，4-ジ-*tert*-ブチルフェニル）ホスファイト（チバ・スペシャルティ・ケミカルズ製の熱安定剤）0.5kgおよび粉状のステアリン酸カルシウム（滑剤）0.4kg、（a-3）成分としてのトリフェニルホスフェート（難燃剤または可塑剤）0.21kgを仕込んで600rpmで混合する。

【0037】内容物温度が70℃に達し、粉立ちがおさまり、粒状になりかかったところで（a-1）PTFEファインパウダー（ダイキン工業製、商品名ポリフロンFA500）を0.25kg投入し、更に5分程度混合を続けた。内容物のほとんどは、直径0.5〜4mm程度の球形類似の粒状物（テトラフルオロエチレンマスターバッチ-1とする。）であった。

#### 【0038】

【製造例2】内容量20リットルのジャケット付きスーパーミキサー（川田製作所製）を用い、70℃の温水でジャケットを加温したところに、（a-2）成分としての粉状のポリフェニレンエーテル1.0kg、トリス（2，4-ジ-*tert*-ブチルフェニル）ホスファイト（チバ・スペシャルティ・ケミカルズ製の熱安定剤）0.5kgおよび粉状のステアリン酸亜鉛0.5kg、（a-3）成分としてのオクタデシル-3-（3，5-ジ-*tert*-ブチル-4-ヒドロキシフェニル）プロピオネート（チバ・スペシャルティ・ケミカルズ製の熱安定剤）0.25kgを仕込んで600rpmで混合する。

【0039】内容物温度が70℃に達し、粉立ちがおさまり、粒状になりかかったところで（a-1）PTFEファインパウダーを0.25kg投入し、更に5分程度混合を続けた。内容物のほとんどは、直径0.2〜1mm程度の球形類似の粒状物（テトラフルオロエチレンマスターバッチ-2とする。）であった。

#### 【0040】

【実施例1】30℃のクロロホルム溶液で測定した $\eta_{sp}/c$ が0.54のポリ-2，6-ジメチル-1，4-フェニレンエーテルを30重量部、ゴム含量約9%の体積平均ゴム粒子径が約1.5μmのゴム補強ポリスチレンを58重量部、トリフェニルホスフェートを11重量部および製造例1のテトラフルオロエチレンマスターバッチ-1を1重量部の割合で、加熱シリンダーの最高温度を300℃に設定したスクリー直径40mmの二軸押出機に供給し、スクリー回転数300rpmで約2

時間連続して溶融混練りした。ストランドを冷却裁断して樹脂組成物ペレットを得た。その間、押出機のダイヘッドには200メッシュのスクリーンを装着したが目詰まりすることなく押出性は良好であった。

【0041】得られた樹脂組成物ペレットを、シリンダー温度240℃および金型温度60℃に設定された型締め圧力80トンの射出成形機により射出成形を行い、物性試験片を得た。以下の試験法により難燃性試験および物性試験を行い、表1の結果を得た。

#### 【0042】（1）難燃性試験

UL-94 垂直燃焼試験に基づき、1/16インチ厚みの射出成形試験片を用いて測定した。ランクV-0が最も優れ、V-1、V-2、HBの順に劣る。

#### 【0043】（2）引っ張り試験

ASTM D638に基づき引っ張り強度および伸度を測定した。

#### 【0044】（3）落錐衝撃試験

50mm×90mm×厚み2.5mmの平板成形片を用い、東洋精機製作所（株）製、商品名、グラフィックインパクトテスターにより落錐衝撃強度としての全吸収エネルギー値（J：ジュール）を測定した。

#### 【0045】（4）外観

射出成形された50mm×90mm×厚み2.5mmの平板を目視判定し、PTFEの分散性を評価した。PTFEの凝集物が見られない場合は○、凝集物が見られる場合は×とした。

#### 【0046】

【実施例2】実施例1において、トリフェニルホスフェートに代えて縮合タイプのリン酸エステル化合物を主成分とするリン系難燃剤（大八化学製、商品名CR741）を14重量部、テトラフルオロエチレンマスターバッチ-1に代えて製造例2のテトラフルオロエチレンマスターバッチ-2を1重量部とした以外は同様にして溶融混練りを行った。スクリーンは目詰まりすることなく押出性は良好であった。得られた樹脂組成物ペレットを、実施例3と同様に評価し、表1の結果を得た。

#### 【0047】

【比較例1】実施例1において、テトラフルオロエチレンマスターバッチ-1に代えて、PTFEファインパウダー（ダイキン工業製、商品名ポリフロンFA500）とステアリン酸カルシウムとの重量比1/4の予備混合物を0.5重量部、二軸押出機に供給し、スクリー回転数300rpmにて溶融混練りした。押出機のダイヘッドには200メッシュのスクリーンを装着したが、混練り開始5分ほどで目詰まりによりダイヘッドの樹脂圧が上昇し、押出運転の継続はできなかった。

【0048】次に、スクリーンを目の粗い40メッシュに代えて押し出し運転することにより、ストランドを冷却裁断して樹脂組成物ペレットを得た。得られたペレットを、実施例1と同様に評価し、表1の結果を得た。

## 【0049】

【比較例2】実施例2において、テトラフルオロエチレンマスターバッチ-1を配合せずに同様に押し出し運転することにより、ストランドを冷却裁断して樹脂組成物ペレットを得た。得られたペレットを、実施例1と同様に評価し、表1の結果を得た。

## 【0050】

【実施例3】ポリブタジエンの含有量15重量%で、スチレン/アクリロニトリル=75/25(重量比)のABS樹脂100重量部に対し、難燃剤としてテトラプロモビスフェノールAを19重量部および三酸化アンチモンを3重量部、熱安定剤としてジブチルスズマレート

を0.5重量部、さらに製造例1のテトラフルオロエチレンマスターバッチ-1を3重量部の割合で、加熱シリ\*ンダーの最高温度を240℃に設定したスクリュウ直径30mmの二軸押出機に供給し、スクリュウ回転数150rpmで約2時間連続して熔融混練りした。ストランドを冷却裁断して樹脂組成物ペレットを得た。その間、押出機のダイヘッドには200メッシュのスクリーンを装着したが目詰まりすることなく押出性は良好であった。

【0051】得られた樹脂組成物ペレットを、シリンダー温度220℃および金型温度60℃に設定された型締め圧力80トンの射出成形機により射出成形を行い、物性試験片を得た。上記試験法により難燃性試験および物性試験を行い、表1の結果を得た。

## 【0052】

## 【表1】

	実施例3	比較例1	比較例2	実施例4	実施例5
押出性					
PTFEの付着 <sup>1)</sup>	無し	多い	—	無し	無し
ダイヘッドの目詰まり	無し	有り	—	無し	無し
物性					
難燃性 ランク	V-1	HB <sup>2)</sup>	V-2	V-1	V-0
滴下	無し	無し	有り	無し	無し
引張強度 (kg/cm <sup>2</sup> )	359	350	347	480	—
伸度 (%)	58	35	62	70	—
落衝撃強度 (J)	41	32	42	40	—
外観	○	×	○	○	○

1) PTFEの付着：フィーダーおよび押出機のホッパー、スクリュウ等へのPTFEの付着凝集。

2) HB：最大燃焼時間が規定の時間以上であった。

## 【0053】

【発明の効果】本発明は、PTFEを熱可塑性樹脂に配合する際の取り扱い上の問題点、すなわち、PTFE同士の凝集、フィーダー、押出機のホッパースクリュー等への付着凝集、押出機ダイヘッドに装着したスクリーン※

※の目詰り等のトラブルを防止し、また、PTFEの分散性を向上したことにより、従来のPTFEを含有する難燃樹脂組成物の特性上の問題点を解決し、燃焼時の滴下防止性、耐衝撃性、外観等に優れた難燃樹脂組成物を提供することができる。

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